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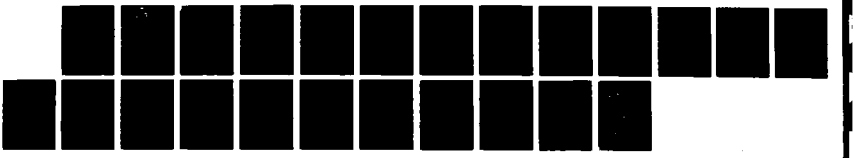

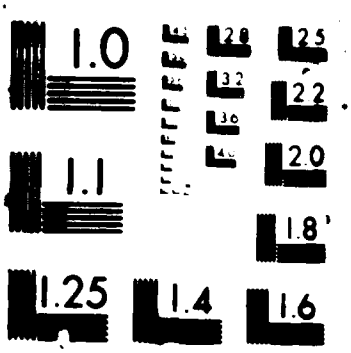
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Major achievements from this research project include the preparation and characterization of new types of dialkylaminophosphorus derivatives and their metal carbonyl complexes. Reductions with $LiAlH_4$ of dialkylaminodichlorophosphines, $R_2NPCl_2$, having sufficiently large dialkylamino groups were found to lead to the corresponding dialkylaminophosphines, $R_2NPH_2$ ($R_2N$ = dicyclohexylamino and 2,2,6,6-tetramethylpiperidino) as very air-sensitive liquids. Dehalogenation of $R_2NPCl_2$ (R = isopropyl or cyclohexyl) with magnesium in tetrahydrofuran was found to give the corresponding cyclotetraphosphines $(R_2N)_4P_4$; the corresponding biphosphines

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$(iPr_2N)_2P_2X_2$ (X = Cl and Br) can be isolated from reactions of $iPr_2NPX_2$ with more limited quantities of magnesium. Reactions of $R_2NPCl_2$ (R = isopropyl, cyclohexyl) with $Na_2Fe(CO)_4$ were found to give the phosphorus-bridging carbonyl derivatives $(R_2NP)_2COFe_2(CO)_6$ as the major products in diethyl ether solution and the triphosphine complexes $(R_2NP)_3Fe_2(CO)_6$ as the major products in tetrahydrofuran solution (R = isopropyl or cyclohexyl). Treatment of $(iPr_2NP)_2COFe_2(CO)_6$ with $NaBH_4$ in methanol was found to result in reduction of the phosphorus-bridging carbonyl group to give the corresponding secondary alcohol $(iPr_2NP)_2CHOHFe_2(CO)_6$. Similar treatment of $(iPr_2NP)_2COFe_2(CO)_6$ with $LiAlH_4$ in diethyl ether was found to result in more extensive reduction to give a product shown by X-ray diffraction to be $(iPr_2NPHCHPNiPr_2)Fe_2(CO)_6$ in which an iron-phosphorus bond has been broken and a new iron-carbon bond formed. Treatment of $(iPr_2NP)_2COFe_2(CO)_6$ with the alkyllithiums RLi (R = Me, nBu) was found to result in addition to the phosphorus-bridging carbonyl group to give the corresponding tertiary alcohols $(iPr_2NP)_2C(R)(OH)Fe_2(CO)_6$. Reactions of $(iPr_2NP)_2COFe_2(CO)_6$ with the alcohols ROH (R = Me, Et) under relatively vigorous conditions result in expulsion of the phosphorus-bridging carbonyl groups to give yellow $(iPr_2NPOR)(iPr_2NPH)Fe_2(CO)_6$. Reactions of the triphosphine complex $(iPr_2NP)_3Fe_2(CO)_6$ with hydrogen halides or with alcohols in the presence of catalytic acetic acid at elevated temperatures were found to result in selective cleavage of the diisopropylamino group attached to the center phosphorus atom of the triphosphine chain to give $(iPr_2NP)_2P(X)Fe_2(CO)_6$ (X = Cl, Br, OMe, OEt). Reactions of $(iPr_2NP)_2P(Cl)Fe_2(CO)_6$ with $NaMn(CO)_5$ and with $(THF)Cr(CO)_5$ give the heterobimetallic derivatives $(iPr_2NP)_2P[Mn(CO)_5]Fe_2(CO)_6$ and $(iPr_2NP)_2P(Cl)[Cr(CO)_5]Fe_2(CO)_6$, respectively. The readily available ligand $(iPr_2N)_2PH$ reacts with $(THF)M(CO)_n$ and with $(THF)Mn(CO)_2C_5H_5$ to give the complexes $(iPr_2N)_2PHM(CO)_n$ (n = 4, M = Fe; n = 5, M = Cr, Mo, W) and $(iPr_2N)_2PHMn(CO)_2C_5H_5$, respectively. In general these $(iPr_2N)_2PH$ complexes react rapidly with the hydrogen halides HX (X = Cl, Br) to cleave selectively in good yield one of the two diisopropylamino groups to give the corresponding $iPr_2NP(H)X$ complexes. Attempts to prepare novel dialkylaminosilicon and dialkylaminoboron derivatives by dehalogenations of $(CH_2)_3(NCMe_3)_2SiCl_2$ and $R_2NBBr_2$ using alkali metals, magnesium, or $(Me_3Si)_2Hg$ did not lead to tractable products in significant quantities.

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FINAL TECHNICAL REPORT

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U.S. Air Force

Bolling Air Force Base, D.C. 20332

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# NOVEL DIALKYLAMINO DERIVATIVES OF PHOSPHORUS AND SILICON

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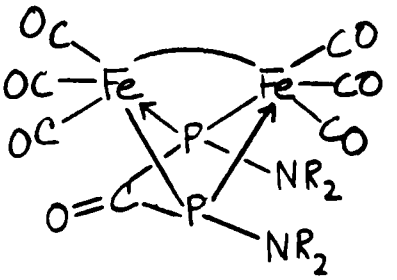
# INTRODUCTION

The original scientific objective of this basic research program was the understanding of the synthesis and chemical reactivity of dialkylamino derivatives of phosphorus and silicon. Such compounds are of potential importance as intermediates in the manufacture of materials of possible value to the Air Force in diverse applications including antioxidants, lubricity agents, elastomers, flame retardants, fuel cell catalysts, thermally stable polymers, and refractory materials.

This project originated from the principal investigator's previous work in synthetic organophosphorus chemistry. His active research in this area was initiated in late 1968 under support from the Air Force Office of Scientific Research. Initial achievements of this project included the development of new methods for preparing chelating polyphosphine ligands which have been used by coordination chemists throughout the world. A more recent project on organophosphorus chemistry, also funded by the Air Force Office of Scientific Research and initiated in early 1981, focused on polyphosphorus compounds containing phosphorus-nitrogen bonds. This project resulted in the discovery of efficient routes for the preparation of certain $(R_2N)_2PH$, $R_2NPH_2$, and $(R_2NP)_4$ derivatives. The studies on the preparation and properties of the latter two types of phosphorus-nitrogen compounds were completed in the initial phases of the current project. The use of $LiAlH_4$ to form the P-H bonds in the syntheses of $(R_2N)_2PH$ and $R_2NPH_2$ derivatives also led to the formation of a novel volatile dialkylaminophosphorus-aluminum hydride derivative, probably $(Et_2N)_2PAlH_4$, which is the focus of a joint proposal by Prof. Michael Norton and the principal investigator on the chemical vapor deposition of aluminum phosphide and other Group III-V materials. This proposal was recently submitted to materials science divisions of the Army Research Office and the Department of Energy.

A productive aspect of this research project arose from merging the principal

investigator's interests in dialkylaminophosphorus chemistry and metal carbonyl chemistry. Numerous unusual types of dialkylaminophosphorus metal carbonyls were prepared and characterized during the course of this research project. The most exciting such compounds were derivatives of the types $(R_2NP)_2COFe_2(CO)_6$ (I: R = isopropyl or cyclohexyl or $R_2N$ = 2,2,6,6-tetramethylpiperidino) containing a novel phosphorus-bridging carbonyl group. Such compounds may be considered to be phosphorus analogues of organic ketones. These compounds are major products from reactions of $Na_2Fe(CO)_4$ with $R_2NPCl_2$ derivatives provided that the $R_2N$ group is sufficiently large and the reaction is carried out in diethyl ether. Furthermore, the reactions of $Na_2Fe(CO)_4$ with $R_2NPCl_2$ derivatives under a variety of conditions yielded a variety of interesting products and in addition raised a number of questions of mechanistic interest. The availability of $(iPr_2NP)_2COFe_2(CO)_6$ (I: R = isopropyl) in 30 gram quantities from a single reaction of $Na_2Fe(CO)_4$ with $iPr_2NPCl_2$ has made this compound available in sufficient quantities for a study of the chemical reactivity of the phosphorus-bridging carbonyl group. Thus ketone-like behavior was noted in the reactions of $(iPr_2NP)_2COFe_2(CO)_6$ with $NaBH_4$ and with alkyllithiums to give alcohols of the type $(iPr_2NP)_2C(R)(OH)Fe_2(CO)_6$ (R = H, Me, nBu, etc.).




I

In terms of scientific publications this research project was very productive leading to 20 publications in major scientific journals and seven presentations at key scientific meetings. Funds for the continuation of aspects of this project involving dialkylaminophosphorus metal carbonyl derivatives are currently being sought from the National Science Foundation.

## NEW RESULTS FROM THIS RESEARCH PROGRAM

### (1) Dialkylaminophosphines, $R_2NPH_2$

Reductions with $LiAlH_4$ of dialkylaminodichlorophosphines,[4] $R_2NPCl_2$, having sufficiently large dialkylamino groups were found to lead to the corresponding dialkylaminophosphines, $R_2NPH_2$ ($R_2N$ = dicyclohexylamino and 2,2,6,6-tetramethylpiperidino), as very air-sensitive liquids characterized by proton and phosphorus-31 NMR spectroscopy.[2,6] These dialkylaminophosphines react with $(THF)M(CO)_n$ (M = Cr and W, n = 5; M = Fe, n = 4) to give the corresponding metal carbonyl complexes $R_2NPH_2M(CO)_n$. The complexes of the type $R_2NPH_2M(CO)_5$ (M = Cr and W) are yellow, sublimable solids, which are considerably more stable than the free $R_2NPH_2$ ligands. Reduction of diisopropylaminodichlorophosphine, $iPr_2NPCl_2$, with $LiAlH_4$ gives a solution shown by phosphorus-31 NMR to contain $iPr_2NPH_2$, but this product decomposes upon attempted isolation. However, the metal carbonyl complexes $iPr_2NPH_2M(CO)_5$ (M = Cr and W) can be isolated as relatively stable yellow sublimable solids by the $LiAlH_4$ reduction of the corresponding $iPr_2NPCl_2M(CO)_5$ complexes.[2,6]

### (2) Tetrakis(dialkylamino)cyclotetraphosphines, $(R_2N)_4P_4$, and Bis(dialkylamino)dihalobiphosphines, $(R_2N)_2P_2X_2$

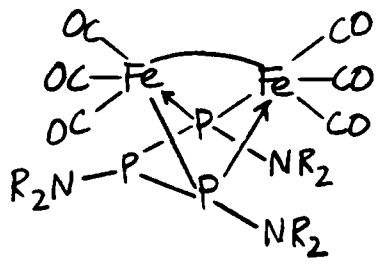
Dehalogenation of $R_2NPCl_2$ (R = isopropyl or cyclohexyl)[4] with magnesium in tetrahydrofuran was found to give the corresponding cyclotetraphosphines $(R_2N)_4P_4$; the corresponding biphosphines $(iPr_2N)_2P_2X_2$ (X = Cl and Br) can be isolated from reactions of $iPr_2NPX_2$ with more limited quantities of magnesium.[5] Dehalogenations with magnesium of $R_2NPCl_2$ derivatives having $R_2N$ groups smaller than diisopropylamino lead to redistribution of the dialkylamino groups giving $(R_2N)_2P\text{-}P(NR_2)_2$ ($R_2N$ = piperidino) or $(R_2N)_3P$ ($R_2N$ = diethylamino or dimethylamino). Such redistribution reactions can be suppressed but not eliminated by using the

homogeneous dehalogenating agent $(Me_3Si)_2Hg$ in hydrocarbon solvents. The steric bulk of the diisopropylamino groups in $(iPr_2N)_4P_4$ reduces its chemical reactivity relative to other cyclotetraphosphines; thus $(iPr_2N)_4P_4$ is unreactive towards oxygen, carbon disulfide, potassium metal, and various metal carbonyls [e.g., $Cr(CO)_6$, $Mo(CO)_6$, and $Fe_2(CO)_9$] under conditions where other cyclotetraphosphines react with these reagents. However, the $P_4$ ring in $(iPr_2N)_4P_4$ is cleaved under mild conditions by hydrogen chloride as well as by bromine and iodine.

(3) Dialkylaminophosphorus Metal Carbonyl Derivatives

Reactions of $R_2NPCl_2$ (R = isopropyl, cyclohexyl) with $Na_2Fe(CO)_4$ were found to give the orange phosphorus-bridging carbonyl derivatives $(R_2NP)_2COFe_2(CO)_6$ (I) as the major products in diethyl ether solution and the orange triphosphine complexes $(R_2NP)_3Fe_2(CO)_6$ (II) as the major products in tetrahydrofuran solution.[8,12,14,15,18,19] The structures of both products (R = isopropyl) have been confirmed by X-ray diffraction.[8,12,14,15] Minor products from the reaction of $iPr_2NPCl_2$ with $Na_2Fe(CO)_4$ in tetrahydrofuran include $(iPr_2NP)_2COFe_2(CO)_6$ (I: R = isopropyl) and the trinuclear derivative $(iPr_2NP)_2Fe_3(CO)_9$ (III: R = isopropyl) as well as orange $(iPr_2NP)_3COFe_2(CO)_6$ shown by X-ray diffraction to have structure IV (R = isopropyl) similar to that of $(iPr_2NP)_3Fe_2(CO)_6$ (II: R = isopropyl) but with a carbonyl group inserted into the triphosphine chain.[12,14,15] Reaction of $Et_2NPCl_2$ with $Na_2Fe(CO)_4$ in diethyl ether gives deep orange $(Et_2NP)_3Fe_3(CO)_{12}$ below 0°C and orange $(Et_2NP)_3Fe_3(CO)_{11}$ at room temperature shown by X-ray crystallography[13,14,15] to have structures V and VI, respectively, arising from migrations of diethylamino groups. Reactions of the binuclear iron carbonyl anion $Na_2Fe_2(CO)_8$ with $R_2NPCl_2$ derivatives (R = methyl, ethyl, isopropyl, cyclohexyl or $R_2N$ = piperidino, 2,6-dimethylpiperidino, 2,2,6,6-tetramethylpiperidino) give the trinuclear derivatives $(R_2NP)_2Fe_3(CO)_9$ (III) and $R_2NPFe_3(CO)_{10}$ (VII). No evidence was obtained for the formation of any $(R_2NP)_2COFe_2(CO)_6$ (I) or $(R_2NP)_3Fe_2(CO)_6$ (II) derivatives in

significant quantities from any of the reactions of $Na_2Fe_2(CO)_8$ with $R_2NPCl_2$ derivatives.[20]



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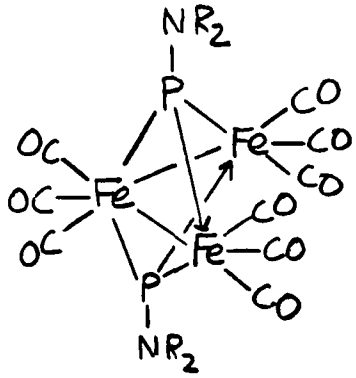

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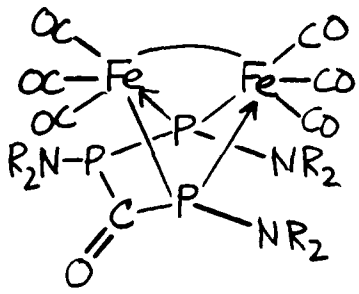

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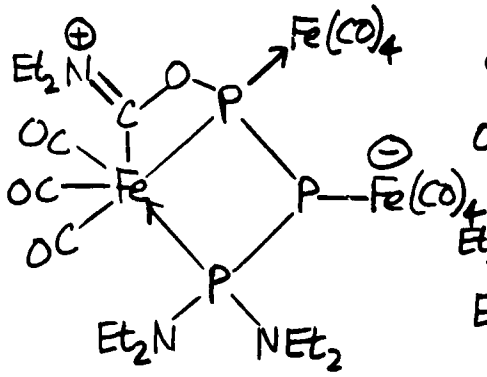

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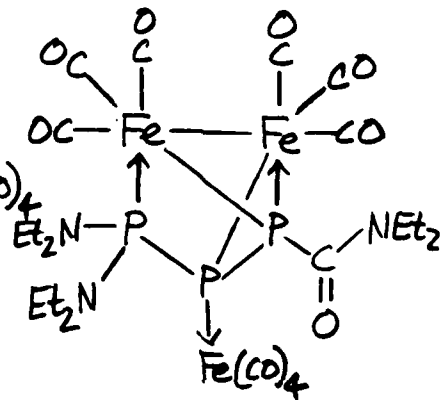

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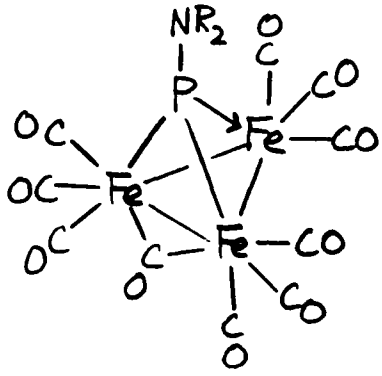
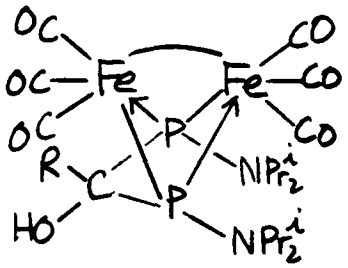


VII

The facile preparation of air-stable $(iPr_2NP)_2COFe_2(CO)_6$ (I: R = isopropyl) in 30 gram quantities from the reaction of $Na_2Fe(CO)_4$ with $iPr_2NPCl_2$ in diethyl ether[8,12,14,15,18] has prompted a detailed study of the chemical reactivity of this compound which is of particular interest because of the presence of the unusual phosphorus-bridging carbonyl group.[8,16] Thus treatment of $(iPr_2NP)_2COFe_2(CO)_6$ (I: R = isopropyl) with $NaBH_4$ in methanol was found to result in reduction of the phosphorus-bridging carbonyl group to give the corresponding secondary alcohol $(iPr_2NP)_2CHOHFe_2(CO)_6$ (VIII: R = H). Similar treatment of $(iPr_2NP)_2COFe_2(CO)_6$ with $LiAlH_4$ in diethyl ether was found to result in more extensive reduction to give a dark orange product of stoichiometry "$(iPr_2NP)_2CH_2Fe_2(CO)_6$" shown, however, by X-ray diffraction to be $(iPr_2NPHCHPNiPr_2)(Fe_2(CO)_6$ (IX) in which an

iron-phosphorus bond has been broken and a new iron-carbon bond formed. Treatment of $(iPr_2NP)_2COFe_2(CO)_6$ with the alkyllithiums RLi (R = Me, nBu) was found to result in addition to the phosphorus-bridging carbonyl group to give the corresponding tertiary alcohols $(iPr_2NP)_2C(R)(OH)Fe_2(CO)_6$ (VIII: R = Me or nBu). Reduction of $(iPr_2NP)_2COFe_2(CO)_6$ with sodium amalgam in tetrahydrofuran results in cleavage of a diisopropylamino group to give the anion $[iPr_2NPCOPFe_2(CO)_6]^-$ which can be isolated as its orange bis(triphenylphosphine)iminium salt or as the light orange trimethyltin derivative $(iPr_2N)(Me_3Sn)P_2COFe_2(CO)_6$ (X) still containing a phosphorus-bridging carbonyl group. Reaction of $[iPr_2NPCOPFe_2(CO)_6]^-$ with $iPr_2NPCl_2$ results in rearrangement with expulsion of the phosphorus-bridging carbonyl group to give orange $[iPr_2NP(iPr_2N)(Cl)PP]Fe_2(CO)_6$



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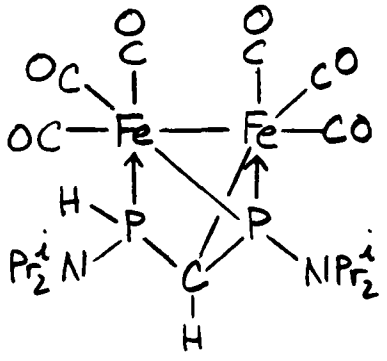

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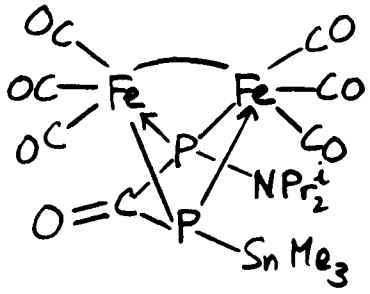

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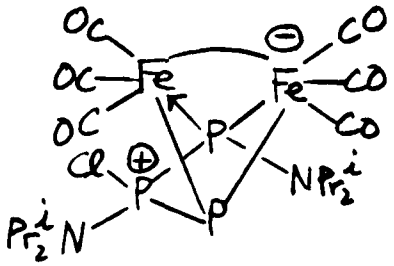
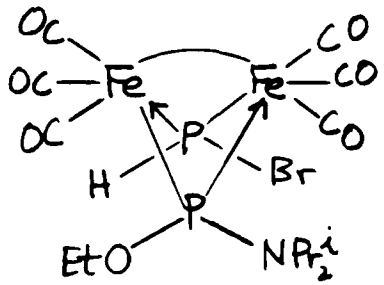


XI

shown by X-ray diffraction to have the unusual structure XI. Reactions of $(iPr_2NP)_2COFe_2(CO)_6$ (I: R = isopropyl) with the alcohols ROH (R = Me, Et) under relatively vigorous conditions results in expulsion of the phosphorus-bridging carbonyl

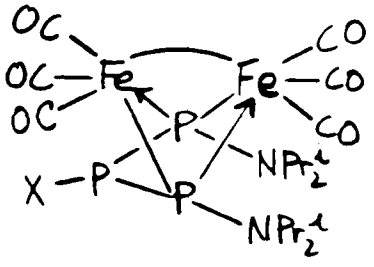
groups to give yellow $(iPr_2NPOR)(iPr_2NPH)Fe_2(CO)_6$. Reaction of $(iPr_2NP)_2COFe_2(CO)_6$ with hydrogen bromide results in expulsion of the phosphorus-bridging carbonyl group and selective cleavage of one of the diisopropylamino groups to give orange $(iPr_2NPBr)(HPBr)Fe_2(CO)_6$; both of the possible stereoisomers of this compound have been detected by phosphorus-31 NMR spectroscopy and one has been isolated in the pure state. Reaction of $(iPr_2NPOEt)(iPr_2NPH)Fe_2(CO)_6$ with hydrogen bromide results in selective cleavage of one of the two diisopropylamino groups to give orange $(iPr_2NPOEt)(HPBr)Fe_2(CO)_6$ shown by X-ray crystallography to have structure XII, which is the first example of a bis(phosphido)hexacarbonyldiiron derivative with four different terminal groups ($iPr_2N$, EtO, H, and Br).




XII

The triphosphine complex $(iPr_2NP)_3Fe_2(CO)_6$ (II: R = isopropyl) is also available in quantity from the reaction of $Na_2Fe(CO)_4$ with $iPr_2NPCl_2$ if the reaction is carried out in tetrahydrofuran rather than diethyl ether.[12,14,15,19] Some studies on the chemical reactivity of this interesting substance were therefore carried out.[12,17] Reactions of $(iPr_2NP)_3Fe_2(CO)_6$ (II: R = isopropyl) with hydrogen halides were found to result in selective cleavage of the diisopropylamino group attached to the center phosphorus atom of the triphosphine chain to give orange $(iPr_2NP)_2P(X)Fe_2(CO)_6$ (XIII: X = Cl, Br). The complex $(iPr_2NP)_3Fe_2(CO)_6$ (II: R = isopropyl) was found to react analogously with the boiling alcohols ROH (R = Me, Et) in the presence of catalytic acetic acid to give orange $(iPr_2NP)_2P(OR)Fe_2(CO)_6$ (XIII: X = OMe, OEt). The derivative $(iPr_2NP)_2P(Cl)Fe_2(CO)_6$ (XIII: X = Cl) is a useful precursor to other

triphosphine diiron hexacarbonyl derivatives through nucleophilic substitution of the chlorine attached to the central phosphorus atom. Thus reaction of $(iPr_2NP)_2P(Cl)Fe_2(CO)_6$ with $NaBH_4$ in tetrahydrofuran solution gives yellow $(iPr_2NP)_2P(H)Fe_2(CO)_6$ (XIII: X = H). However, reduction of $(iPr_2NP)_2P(Cl)Fe_2(CO)_6$ with $LiAlH_4$ results in phosphorus-phosphorus bond cleavage to give yellow $(iPr_2NPH)_2Fe_2(CO)_6$. Nucleophilic substitution of the chlorine atom of $(iPr_2NP)_2P(Cl)Fe_2(CO)_6$ (XIII: X = Cl) with $NaMn(CO)_5$ provides a route to the new heterobimetallic derivative $(iPr_2NP)_2P[Mn(CO)_5]Fe_2(CO)_6$ (XIII: X = $Mn(CO)_5$). The heterobimetallic derivatives $(iPr_2NP)_2P(Cl)[Cr(CO)_5]Fe_2(CO)_6$, $(iPr_2NP)_2P(H)[Cr(CO)_5]Fe_2(CO)_6$, and $(iPr_2NP)_2P(H)[Fe(CO)_4]Fe_2(CO)_6$ can be obtained by complexation of the central phosphorus atoms in $(iPr_2NP)_2P(X)Fe_2(CO)_6$ (XIII: X = H, Cl) with $(THF)Cr(CO)_5$ and $Fe_2(CO)_9$/THF.[17]

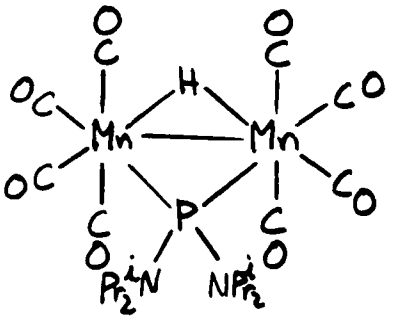



XIII

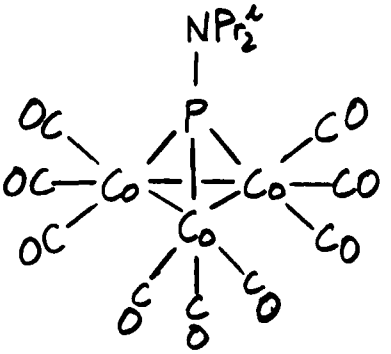
The readily available bis(dialkylamino)phosphine, $(iPr_2N)_2PH$, is an interesting ligand for metal carbonyl chemistry since after complexation the phosphorus-nitrogen bonds can be selectively cleaved by acidic reagents to give metal carbonyl complexes of organophosphorus ligands not available in the uncomplexed state.[1,7,9,10,11] The complexes $(iPr_2N)_2PHM(CO)_n$ (n = 4, M = Fe; n = 5, M = Cr, Mo, W) and $(iPr_2N)_2PHMn(CO)_2C_5H_5$ are obtained as air-stable sublimable hydrocarbon-soluble solids by reactions of $(iPr_2N)_2PH$ with the corresponding tetrahydrofuran complexes $(THF)M(CO)_n$ and $(THF)Mn(CO)_2C_5H_5$.[1,9] In general these $(iPr_2N)_2PH$ complexes react rapidly with the hydrogen halides HX (X = Cl, Br) to cleave selectively in good

yield one of the two diisopropylamino groups to give the corresponding $iPr_2NP(H)X$ complexes; the exception to this reactivity pattern is the reaction of $(iPr_2N)_2PHMn(CO)_2C_5H_5$ with HBr, which proceeds all the way to $Br_2P(H)Mn(CO)_2C_5H_5$. Dehydrochlorination of $iPr_2NP(H)ClFe(CO)_4$ with excess triethylamine gives a low yield of the phosphorus-bridging carbonyl derivative $(iPr_2NP)_2COFe_2(CO)_6$ (I: R = isopropyl) discussed in detail above.[9]

The reactions of $(iPr_2N)_2PH$ with the metal-metal bonded metal carbonyls $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ have been shown to follow a different course than those outlined above.[3,10] Thus, photolysis of $(iPr_2N)_2PH$ with $Mn_2(CO)_{10}$ in tetrahydrofuran solution results in cleavage of the phosphorus-hydrogen bond to give yellow air-stable sublimable $[\mu\text{-}(iPr_2N)_2P](\mu\text{-}H)Mn_2(CO)_8$ shown by X-ray diffraction to have structure XIV in which a manganese-manganese bond in bridged symmetrically by both a hydrogen atom and a bis(diisopropylamino)phosphido group. One of the two diisopropylamino groups in XIV is selectively cleaved with the hydrogen halides HX (X = Cl, Br) to give the corresponding complex $(\mu\text{-}iPr_2NPX)(\mu\text{-}H)Mn_2(CO)_8$ shown by its infrared $\nu(CO)$ and NMR spectra to have a structure analogous to XIV. Reaction of $(iPr_2N)_2PH$ with $Co_2(CO)_8$ in hexane at ambient temperature gives a complex mixture of relatively unstable products from which paramagnetic (2.0 $\mu_B$) black air-sensitive crystalline $(\mu_3\text{-}iPr_2NP)Co_3(CO)_9$ can be isolated after chromatography on silica gel. X-ray crystallography on this complex indicates the expected structure XV with a $PCo_3$ tetrahedron.[3,10]

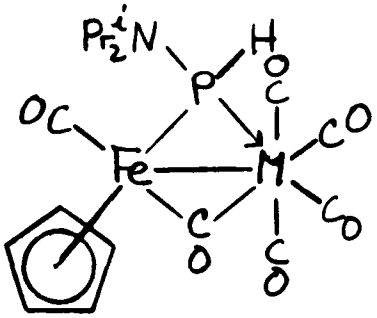


XIV

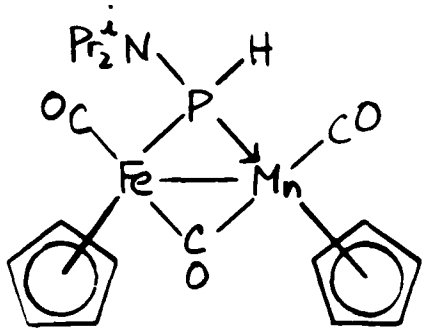


XV

The reactivity of the phosphorus-halogen bonds in the $iPr_2NP(H)XM(CO)_n$ derivatives towards nucleophiles provides a novel approach for the synthesis of interesting heterobimetallic derivatives.[7,11] Thus reactions of $iPr_2NP(H)XM(CO)_5$ (X = Br, M = Cr; X = Cl, M = Mo, W) and $iPr_2NP(H)ClMn(CO)_2C_5H_5$ with $NaFe(CO)_2C_5H_5$ result in nucleophilic substitution of the phosphorus-bonded halogen with the iron nucleophile to give relatively good yields of deep orange $C_5H_5Fe(CO)_2PH(NiPr_2)M(CO)_5$ and deep red $C_5H_5Fe(CO)_2PH(NiPr_2)Mn(CO)_2C_5H_5$, respectively, which do not contain metal-metal bonds. Photolyses of $C_5H_5Fe(CO)_2PH(NiPr_2)M(CO)_5$ (M = Cr, W) and $C_5H_5Fe(CO)_2PH(NiPr_2)Mn(CO)_2C_5H_5$ in pentane or cyclohexane solution result in rapid decarbonylation to give black $C_5H_5FeM(CO)_6PH(NiPr_2)$ (M = Cr, W) and $(C_5H_5)_2FeMn(CO)_3PH(NiPr_2)$, respectively. X-ray diffraction of $C_5H_5FeM(CO)_6PH(NiPr_2)$ (M = Cr, W) indicates structures of the type XVI (M = Cr, W) in which a heteronuclear Fe-M bond is bridged by both a carbonyl group and a $iPr_2NPH$ phosphido group. A related structure XVII is postulated for $(C_5H_5)_2FeMn(CO)_3PH(NiPr_2)$ on the basis of the observation of two terminal and one bridging $\nu(CO)$ frequencies.




XVI




XVII

(4) Dialkylaminosilicon Derivatives

The general objective of this portion of the project was the preparation of cyclic derivatives of the stoichiometry $[(R_2N)_2Si]_n$. In this connection attempts to dehalogenate $(CH_2)_3(NCMe_3)_2SiCl_2$ (XVIII) and $R(iPr_2N)SiCl_2$ led to the following observations:

(a) $(CH_2)_3(NCMe_3)_2SiCl_2$: This dichlorosilane did not appear to react with magnesium metal (boiling tetrahydrofuran), lithium metal (boiling tetrahydrofuran), sodium metal (boiling toluene), $(Me_3Si)_2Hg$ (pentane at room temperature), $LiAlH_4$ (diethyl ether at room temperature), and $Na_2Fe(CO)_4$ (tetrahydrofuran at room temperature). Reactions of $(CH_2)_3(NCMe_3)_2SiCl_2$ (XVIII) with potassium metal in boiling tetrahydrofuran gave a mixture of unidentified products apparently resulting from cleavage of one or both silicon-nitrogen bonds. Reaction of $(CH_2)_3(NCMe_3)_2SiCl_2$ with sodium naphthalenide in boiling tetrahydrofuran gave a mixture of unreacted starting material and unidentified products incorporating the naphthalene.

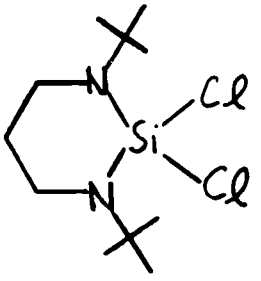
(b) $Me(iPr_2N)SiCl_2$: This dichlorosilane did not appear to react with lithium metal in tetrahydrofuran or with $(Me_3Si)_2Hg$ in a mixture of pentane and hexane. Reactions of $Me(iPr_2N)SiCl_2$ with sodium or potassium metal under various conditions appeared to give complex mixtures from which tractable products of interest could not be isolated.

From these experiments the following general conclusions can be drawn:

(a) The introduction of dialkylamino substituents into chlorosilanes makes them very difficult to dehalogenate.

(b) The silicon-nitrogen bond is too readily cleaved to allow forcing conditions for reactions of dialkylaminochlorosilanes with very strong reducing agents.

(c) In some reactions ether solvents such as tetrahydrofuran or diethyl ether are cleaved in significant amounts.




XVIII

These negative results suggested that reactions of $HSiCl_3$ and $H_2SiCl_2$ with

secondary amines might provide better entries for the preparation of cyclic $[(R_2N)_2Si]_n$ derivatives. In this connection the reaction of $HSiCl_3$ with excess diisopropylamine in boiling hexane was found to give $(iPr_2N)_2SiHCl$ as an air-sensitive colorless liquid, b.p. 112°/1mm. An attempt to prepare $(iPr_2N)_2SiFe(CO)_4$ by reaction of $(iPr_2N)_2SiHCl$ with $Fe_2(CO)_9$ did not appear promising and unreacted $(iPr_2N)_2SiHCl$ was identified as the only hexane-soluble silicon compound in the reaction mixture.

We also investigated replacement of the chlorine atoms in $(CH_2)_3(NCMe_3)_2SiCl_2$, $PhMeSiCl_2$, and $Me(iPr_2N)SiCl_2$ with trimethylsilyl groups through reaction with the $LiSiMe_3$ obtained by treatment of $(Me_3Si)_2Hg$ with lithium metal in a hydrocarbon solvent in order to provide intermediates for the preparation of $[(R_2N)_2Si]_n$ derivatives by subsequent photolytic elimination of hexamethyldisilane or trimethylsilane. Mass spectrometric evidence was obtained for the formation of $(CH_2)_3(NCMe_3)_2Si(H)SiMe_3$ and $Me(iPr_2N)Si(SiMe_3)_2$ from reactions of this type, but these compounds were not obtained in useful quantities for further chemistry.

(5) Dialkylaminoboron Derivatives

The general objective of this portion of the research project was the preparation of cyclic dialkylaminoboranes of the general formula $(R_2NB)_n$ by the dehalogenation of corresponding dialkylaminodihaloboranes. Cyclic dialkylaminoboranes are of potential interest as precursors both to novel boride refractory materials as well as for more efficient syntheses of polyhedral boranes and carboranes for ingredients in high energy materials and high temperature polymers.

Our studies on the dehalogenation of $R_2NBX_2$ compounds with strong reducing agents can be summarized as follows:

(a) Reaction of $Et_2NBBr_2$ with excess sodium in boiling toluene gave a liquid product suggested by mass spectrometry to contain cyclic derivatives of the stoichiometries $(Et_2NB)_n$ (n = 4, 5, 6, 7). This mixture did not form a chromium carbonyl complex upon reaction with norbornadienetetracarbonylchromium. A similar reaction of

$Et_2NBBr_2$ with sodium in boiling hexane led to redistribution of diethylamino groups to give $(Et_2N)_3B$ and $(Et_2N)_3B{\cdot}NHEt_2$.

(b) Treatment of $R_2NBBr_2$ (R = isopropyl or $R_2N$ = 2,2,6,6-tetramethylpiperidino) with sodium amalgam at room temperature resulted only in recovery of the starting material.

(c) Reaction of $Et_2NBBr_2$ with $(Me_3Si)_2Hg$ in toluene solution at low temperatures resulted in a low yield of a complex mixture of products which could not be separated or conclusively identified.

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(2) King, R. B.; Fu, W.-K.; Holt, E. M. "Novel Metal Carbonyl Complexes from Bis(diisopropylamino)phosphine," presented by R. B. King at the Twelfth International Conference on Organometallic Chemistry, Vienna, Austria, September, 1985: abstracts, p. 341.

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